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(54) **Process and device to improve the performances and the life, with corrosion reduction, in Kettle type carbamate condensers in urea plants.**

(57) A process to improve the performances and reduce the effects of corrosion in vapour stripping condensations in urea plants, through the use of a carbamate condenser with "Kettle"-type tube sheet.

Characteristically in the zone facing the pipe inlet of said condenser, the condensation of a notable portion of stripping vapours takes place.

The devices used to put said process into operation comprise in the zone facing the tube sheet of the carbamate condenser: a) a feed opening containing at least: a1) a return pipe of the condensed carbamate solution, a2) an ejector for the mixing of the recycle liquid with the solution rich in water coming from the outside of said feed opening, and a3) an outlet for the condensed fluid flowing toward the reactor, being the nozzle of said return pipe positioned in the periphery of the tube sheet's discharge zone; b) at least a conduct for the stripping vapours internally or externally crossing the condenser and having the outlet at the periphery of the inflow of the tube sheet.

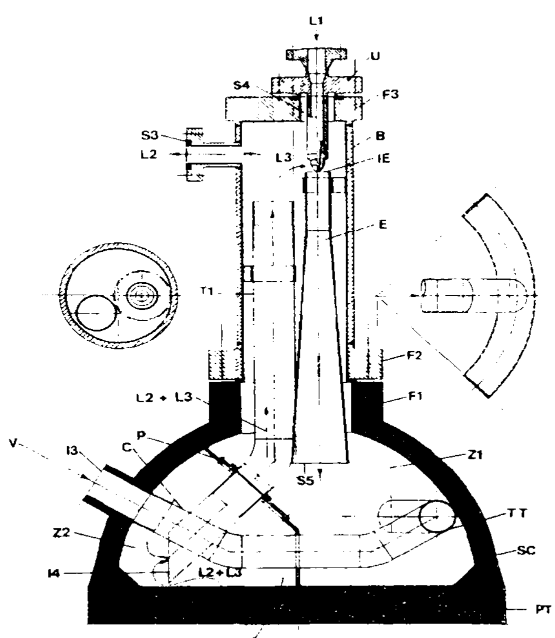

FIG. 2

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The present invention relates to a process to improve the performances and to reduce the corrosion effects in high pressure and temperature condensation of the NH_3, CO_2, H_2O vapours, which are generated in the treatment systems, so-called of stripping, of the solution coming from the urea reactor, said condensation being carried out by means of a carbamate condenser in particular of the tube bundle "Kettle" type to which part of the carbamate solution effluents from the condenser itself is recycled.

As known in modern urea plants characterized by the isobaric stripping of most of the unreacted substances contained in the urea solution outflowing the reactor and which utilize as stripping agents part of the CO_2 or NH_3 feed stream, the so-obtained stripping vapours are condensed in suitable heat exchangers recovering the heat produced in said condensation with low pressure steam production (4÷5 bar a).

Regarding the condensation, it is necessary to feed the condenser with the carbamate solution coming from the downstream distillation section and containing enough water to keep the carbamate in solution too.

The carbamate condensers of particular interest are horizontal U-tube heat exchangers, better known as horizontal Kettle condensers usually utilized in the urea plants based on the Snamprogetti process.

This condensation stage is extremely critical and requires a complicated combination of operative parameters: it is in fact essential that the vapours to be condensed (NH_3, CO_2, H_2O) are finely mixed to the carbamate solution rich in water, which acts as absorbing agent, and comes from the section downstream the synthesis section, so that a high temperature condensation can take place producing therefore steam at the highest possible pressure; moreover it is necessary to protect the components (the condenser exchange surface), usually in stainless steel for costs reduction, from corrosion, being the process fluids very corrosive.

Unfortunately, the Kettle condensers, commonly used in modern plants too, denotes big life limitations and cannot assure optimal operative conditions, being based on processes which have various limitations and drawbacks, among them are cited:

- The separation (or segregation), at the condenser's pipe nozzle, of liquid-vapour components with consequent accumulation of vapours in the upper portion of the tube sheet of tube bundle and liquid in the lower portion of said sheet.

  This separation is caused by the low velocity of the fluids' circulation (approx. 0.1 m/sec.) and by the great difference in specific weight between liquid and vapour.

  Consequently, the vapour/liquid ratio in the zone facing the tube sheet and in most of the pipes shall not be optimal, and shall concensate with difficulty.

  To obviate this problem, it is necessary to notably increase the exchange surface, with incrementation of the size of the device and also of the cost for the same.

  In addition, the separation of the liquid-vapour components cause a lowering of the thermal level of the steam produced with respect to the amount theoretically producible.
- The corrosion of the tube sheet and the tubes (the exchange surface of the condenser in general) caused by the above mentioned separation of the two phases.

  One of the precautions normally undertaken to contain the negative effects of the phenomena is to introduce, for example, air into the system, which will reach the carbamate condenser through the stripping vapours to be condensed. It is, nevertheless, indispensable to guarantee a uniform passivation in all areas of the equipment avoiding zones with stagnant liquid or liquid circulating at a velocity insufficient to guarantee the necessary contribution of passivation oxygen (dead spots, creation of high temperature zones).
- An imperfect distribution of passivating air as described above that, being contained in the vapours, will tend to privilege the upper tubes of the carbamate condenser with respect to the lower ones.

Methods have been proposed, for example in the second integration of the Italian Patent Application No. 23214, in which is described a horizontal tube bundle condenser with recirculation outside the condenser of part of the carbamate solution effluent for the same apparatus this system being studied to solve the critical aspect of mixing of the absorption liquid and the vapors to be condensed in order to ensure an optimial distribution (steeping) of the liquid-steam mixture on the inside of the pipes of said condenser, that only partially and in an insatisfactory way solve the problems present in the above mentioned equipment.

From here the importance of improving in a definitive way the performances and duration, with corrosion reduction in the carbamate condensers of Kettle type.

The first aim of the invention is to provide a process in which the above mentioned inconveniences are eliminated and a higher thermal level of produced steam is obtained, as well as a higher

carbamate condensation, thus notably improving the performances and life of the equipment.

This aim and others still shall be better explained in the description that follows, are obtained through a process according to the invention described in the description introduction and Claim 1, that is characterized by the fact that in the zone facing the inlet of the tubes of said condenser the condensation of a large portion of stripping vapours is carried out and the pressure drop at the outlet of said tubes is increased.

The devices to carry out the process, according to the previous claims, are characterized by the fact that they comprise of, in the zone facing the condenser tube sheet: a) a device containing at least: a1) a return pipe of the condensed carbamate solution, a2) an ejector for the mixing of the recycle liquid with the solution rich in water coming from the outside of said part, and a3) an outlet of condensed fluid going to the reactor, being the entrance of said return positioned in the peripherical part of the tube sheet deflux zone; and b) at least a stripping vapour duct passing the condenser externally or internally and having the outlet at the peripherical part of the tube sheet influx zone to the tube sheet, being the vapour distribution effected by means of a perforated torus portion.

Another particular form of the devices according to the invention is characterized by the fact that, when the Kettle-type carbamate condenser is vertical, the recycle of the carbamate inside the said zone facing the tube sheet is with thermosiphon circulation.

There are many advantages of operating in this manner, which are clearly shown in the following description.

The formation of carbamate in the operating conditions of the condenser are related more to the system's capacity to absorb the high reaction heat developed than to its kinetic nature; the higher this capacity is, the easier the formation of carbamate shall be.

In the zone preceding the tube inlet of the condenser, where the cold carbamate solution rich with water and hot vapours to be condensed come into contact, an almost instant reaction between the NH_3 and CO_2 takes place with formation of carbamate.

The adiabatic reaction is interrupted when the solution's temperature shall be in equilibrium with the vapour phase.

As a result there is a carbamate precondensation of a small portion of the CO_2, while the remaining portion shall be condensated in the condenser's tubes with the problems mentioned above.

In this particularly simple and advantageous way according to the process and the devices claimed, it is possible, being the recycle solution colder than the carbamate solution rich in water and therefore enabled to absorb heat, to notably increase the formation of carbamate in the zone facing the conderser tubes' inlet.

Among the many results obtained, we limit citing:

- a notable increase of liquid flow rate to the tubes;
- an elevated reduction of the vapours flow rate to the tubes;
- a consequent drastic reduction of the vapour/liquid ratio in the zone facing the tube inlet of the condenser.

Thanks to the higher liquid flow rate and the consequent higher pressure drop at the nozzle, it shall be possible to obtain a more uniform distribution of the fluids at the entrance of the tube sheet and inside the tubes, obtaining a higher thermal exchange coefficiency and a better vapours distribution, and therefore in the passivation air throughout the entire condenser, with practical elimination of the above mentioned corrosion phenomena. In addition, thanks to the higher thermal exchange coefficiency, it shall be possible to raise the thermal level of the steam produced.

The portion of pre-condensed carbamate in the zone facing the tube sheet, can be advantageously varied in order to obtain an almost complete condensation of the stripping vapours in the said zone preceding the pipes' inlet of the condenser.

Optimal results are, however, reachable limiting the above mentioned pre-condenser to a liquid/vapour weight ratio between 4 and 46, better between 4 and 20 and perferably between 5 and 10; in this way the ratio between recycle liquid and the carbamate solution rich in water is maintained in the interval between 4 and 30, better between 6 and 15 and better again between 6 and 10.

Is it particularly surprising how the inconveniences mentioned above can be brilliantly and simply resolved by modifying the Kettle type carbamate condenser already existing according to the present invention.

The different aspects and advantages of the invention are better shown in the detailed description of an example using references from the attached drawings, example given without any limitation to the invention, and in which :

- Figure 1 is a sketch of a section with partial axial schematic planes of a Kettle horizontal tube sheet condenser of traditional type;
- Figure 2 is a sketch of a section with partial axial schematic planes of the zone facing the tube sheet of the Kettle exchange of horizontal type with the indication of new devices according to a perferred version;

- Figure 3 is a sketch of a section with partial axial schematic planes of a Kettle condenser of vertical type having a carbamate recycle inside the zone facing the tube sheet with thermosiphon circulation.

In particular, in Figure 1 a heat exchanger SC is shown, of horizontal Kettle tube sheet type with "U" pipes coming from a tube sheet PT at the inlet of the condenser SC, tube sheet that separates the tubes Ti from the influx zone Z1 and the discharge zone Z2 of the liquid-steam mixture, and then separate impermeabilized from the wall P.

The carbamate solution rich in water L1 coming from the distillation section downstream (not shown), and the stripping vapours V, flow together through the nozzle I1 in the chamber Z1, where they mix before they enter the tubes Ti, through the nozzle I2 of the tube sheet, from which they flow down through the outlet S1 of PT to then exit from the device, after having crossed Z2, through the opening S2.

The water for the thermal exchange is fed to the exchanger through line 10 and is collected in the form of acqueous vapour in line 11.

Figure 2 shows, in a detailed way, the portion facing said tube sheet PT of the exchanger SC, with the two zones Z1 and Z2 separate and impermeabilized from the wall P. To the flange F1 of said exchanger SC a feed opening B is connected with flanged ends F2, F3, sized to contain a return pipe T1 and an ejector E. The feed opening B is equipped with an outlet S3 for the condensed solution L2 to be sent to the reactor, and with an opening S4 for the insertion of an ejector nozzle U.

A conduct C is also foreseen to internally cross the zone Z1 and Z2, and with end terminating as torus section TT situated in the periphery of zone Z1 for an optimal dispersion of stripping vapours V which have entered from opening I3 of said conduct C.

The carbamate solution rich in water L1 (motor fluid) enters through the ejector nozzle U into B, is mixed at the opening IE of the ejector E with the recycle carbamate solution L3, and then enters from S5 into the zone Z1, where it comes into intimate contact with the stripping vapours V favouring the pre-condensation, before crossing the tube sheet PT.

The condensated mixture L2 + L3 effluent PT enters in the opening I4 of the return pipe T1, put on the periphery of zone Z2 to avoid the accumulation of inerts (dead sacks), and is in part recycled (L3) on the inside of the condenser itself and in part (L2) sent to the synthesis reactor upstream (not shown).

Figure 3 shows a Kettle-type carbamate condenser with vertical tube bundle evidencing the thermosiphon circulation of the carbamate recycle inside the zone facing the tube sheet.

The references used in Figure 1 and 2, and also shown in Figure 3, all obviously have the same significance.

The comparative example described hereunder, in which a traditional type of Kettle condensator is compared (as shown in Figure 1) to a classic Kettle condenser modified according to the process and the claimed devices (see Figure 2), show the advantages of the invention better.

Comparative Example

In the normal assett of Figure 1, 25'000 Kg/h of carbamate solution L1 enter through I1 at 76 °C and 150 bar having the following composition:

NH_3	47.12 % weight
CO_2	17.46 % weight
H_2O	35.42 % weight

and 50'000 Kg/h of vapours V at 190 °C and 150 bar, and having the following composition:

NH_3	56.74 % weight
CO_2	32.60 % weight
H_2O	10.66 % weight

In the mixer Z1 the two fluids are mixed with a partial condensation of the vapours (approx. 18% of the vapours condense raising the temperature of the liquid phase to 170 °C).

At the tube inlet I2), there are the following flow rates :

liquid	: ≈ 34'000 Kg/h
vapour	: 41'000 Kg/h

The liquid/vapour weight ratio at the pipe inlet is 0.83.

In particular, in the chamber Z1 approx. 33% of the vapours condense and the temperature increases up to 175 °C.

At the pipe inlet of the condenser there are the following flow rates:

liquid	: 191'700 Kg/h
vapour	: 33'300 Kg/h

with a liquid/vapour weight ratio equal to 5,75, approx. 7 times that of the run without internal recycle.

It is this notable increase of the liquid phase with respect to the vapour phase that ensures a more uniform distribution of the two phases in the exchanger's pipes, eliminating at the origin the cause of malfunctions previously complained about.

Claims

1. Process to improve the performances and to reduce the corrosion effects in high pressure and temperature condensation of the NH_3, CO_2, H_2O vapours, which are generated in the treatment systems, so-called of stripping, of

the solution coming from the urea reactor, said condensation being carried out by means of a carbamate condenser in particular of the tube bundle "Kettle" type to which part of the carbamate solution effluents from the condenser itself is recycled, characterized by the fact that in the zone in front of the tubes inlet of said condenser the condensation of a large portion of the stripping vapours is carried out and, the pressure drop (at the entrance of said tubes) is increased.

2. Process according to claim 1, characterized by the fact that the weight ratio liquid/vapour weight ratio at the entrance of the condenser tubes is between 4 and 46, better between 4 and 20 and preferably between 5 and 10.

3. Process according to claim 1, characterized by the fact that the ratio between the recycle solution and the carbamate solution rich in water is maintained in the range between 4 and 30, better between 6 and 15 and even better between 6 and 10.

4. Process according to claim 1, characterized by the fact that the recycle of part of the carbamate solution effluent from the condenser occurs in its interior.

5. Process according to the claims 1 and 4, characterized by the fact that, when the Kettle carbamate condenser is vertical, the carbamate recycle internal to said zone in front of the tube sheet is of the thermosiphon type.

6. Devices for carrying out the process, according to the previous claims, for the improvement of the performances and the reduction of the corrosion effects in the carbamate condensers, of the tube bundle "Kettle" type, with recycle in the condenser of part of the carbamate solution effluents from the apparatus, said condensers including a condensation chamber with tube bundle having "U" tubes departing from a tube sheet at the condenser inlet, characterized by the fact of comprising in the zone in front of said tube sheet: a) a device containing at least: a1) a return pipe of the condensed carbamate solution, a2) an ejector for the mixing of the recycle liquid with the solution rich in water coming from the outside of said part, and a3) an outlet of the condensed fluid going to the reactor, being the entrance of said return pipe positioned in the peripherical part of the tube sheet deflux zone; b) at least a stripping vapours duct passing externally or internally the condenser, and having the outlet in the peripherical part of the tube sheet influx zone, being the vapours distribution carried out by means of a perforated torus portion.

7. Devices according to claim 6, characterized by the fact that, when the Kettle carbamate condenser is vertical, the carbamate recycle internal to said zone in front of the tube sheet is with thermosiphon circulation.

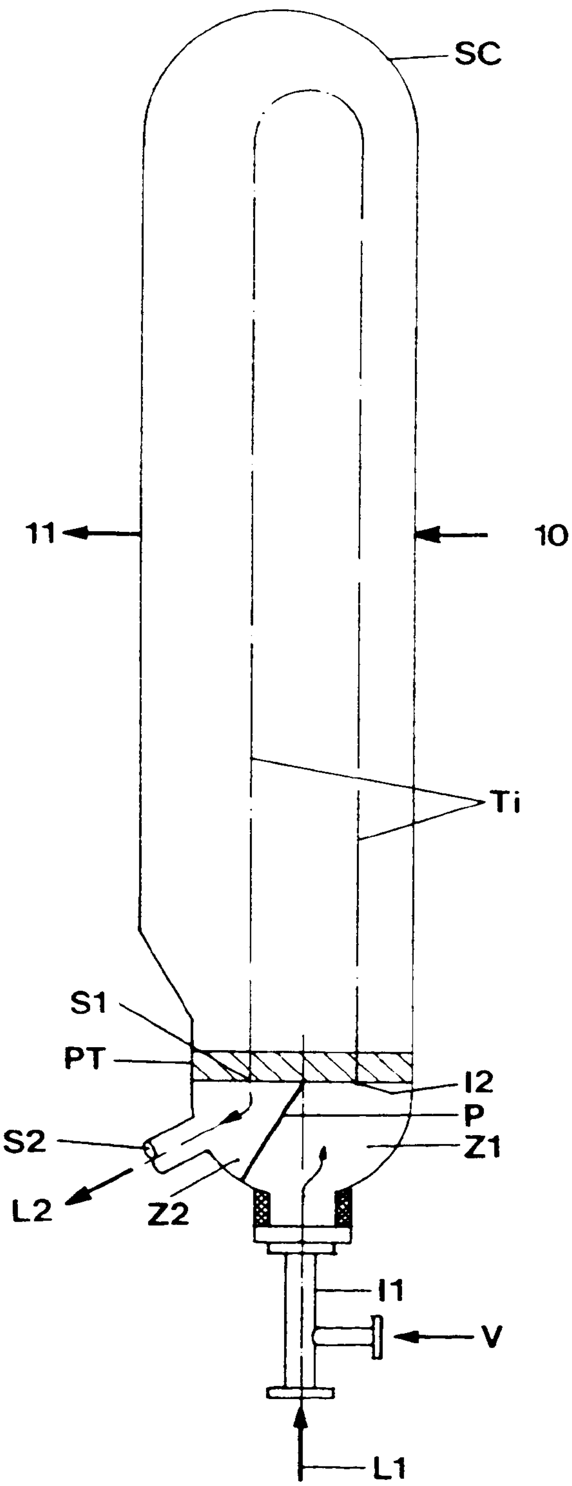
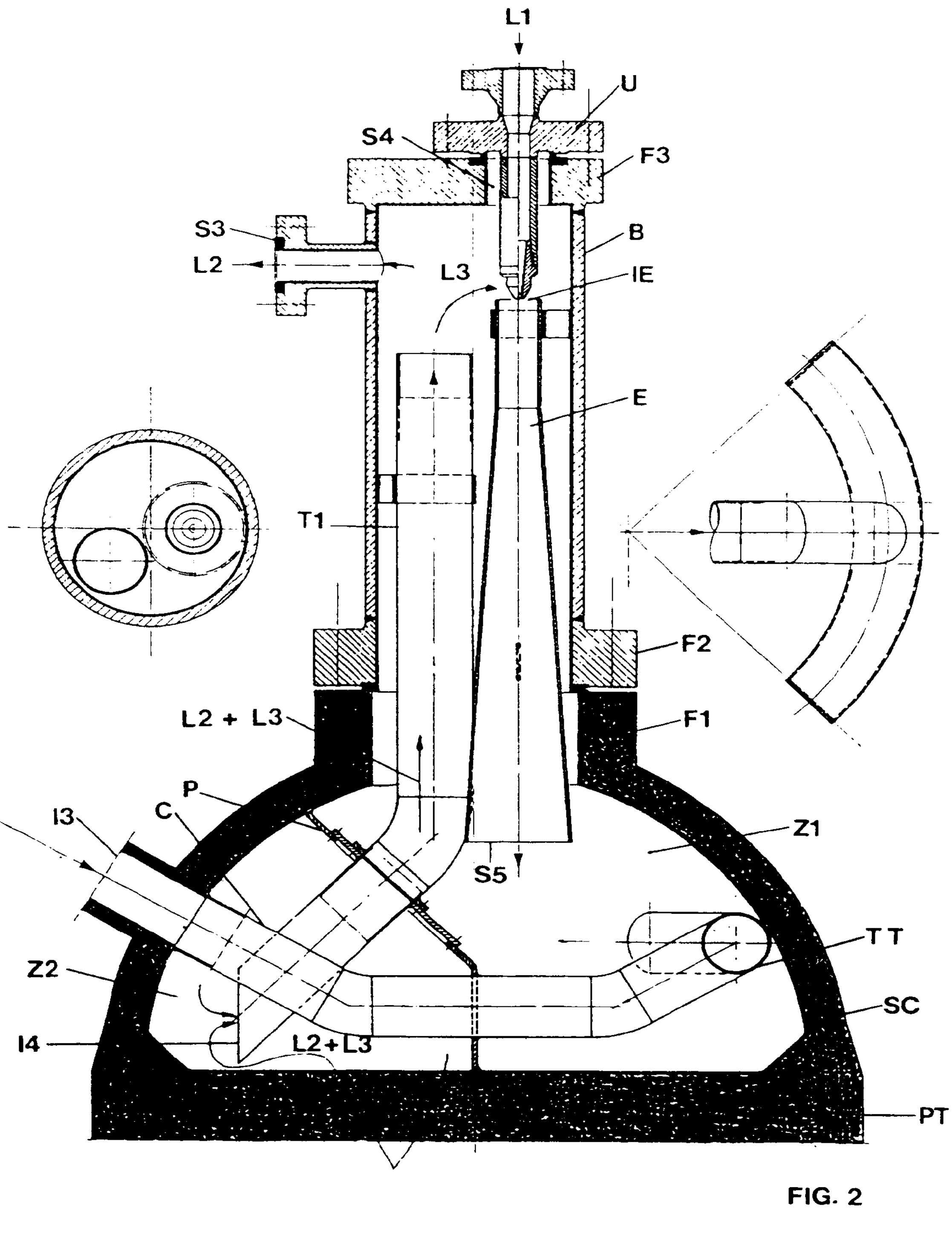


FIG. 1


L1
U
S4
F3
S3
B
L2
L3
IE
E
T1
F2
L2 + L3
F1
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C
Z1
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T T
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SC
I4
L2+L3
PT

FIG. 2

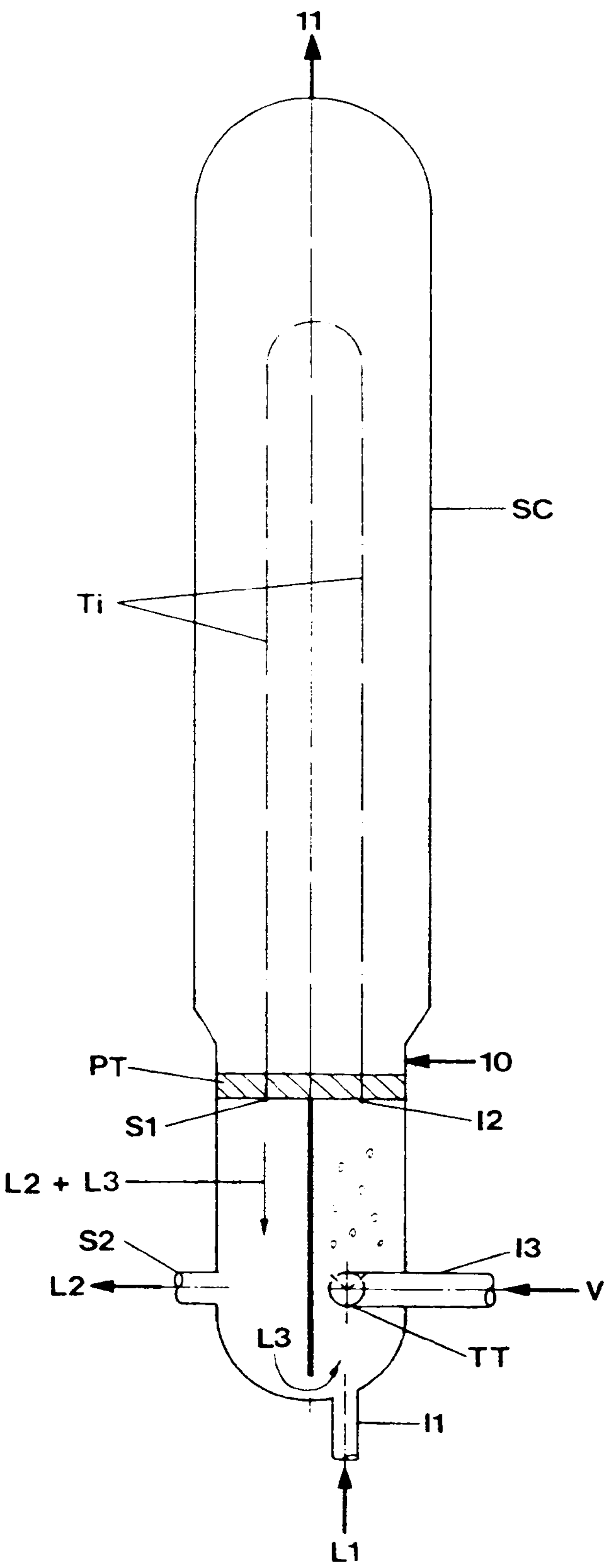

FIG. 3

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 10 3159

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	FR-A-2 308 615 (SNAMPROGETTI) * Example; figure 2; claims * – – –	1-7	C 07 C 273/04
A	GB-A-2 157 687 (SNAMPROGETTI) * The whole document * – – –	1-7	
A	EP-A-0 002 298 (UNIE VAN KUNSTMESTFABRIEKEN) * Figure; claims * – – – – –	1-7	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)
C 07 C 273/00 B 01 D 5/00

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	12 September 91	ZERVAS B.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same catagory
A : technological background
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
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Korrektur einer Patentanmeldung / Correction of a Patent Application / Rectification d'une demande de brevet

Verweis auf die Berichtigung im Dokument Nr.: / Notification regarding the correction of document no. / Avis de correction du document n°

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Veröffentlichungsdatum: / Date of publication: / Date de la publication

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Korrekturhinweis im Patentblatt Nr. / Mention of correction in Patent Bulletin No. / Mention de la correction dans le bulletin n° **94/12** veröffentlicht am / published on / publié le **23039**

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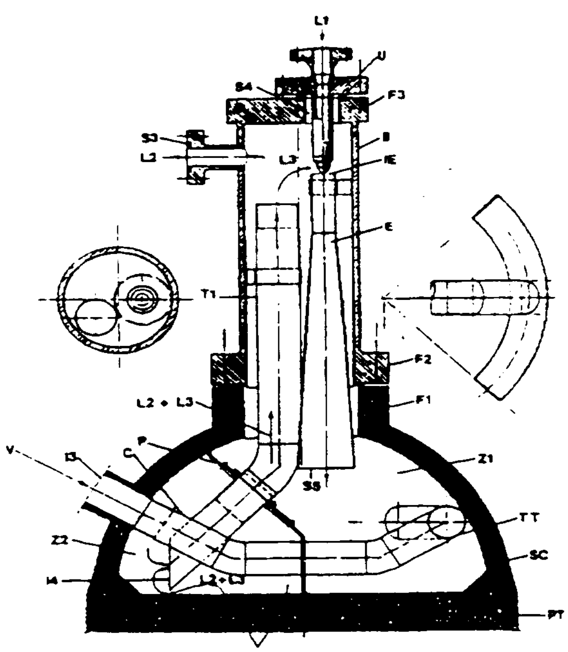

FIG. 2

Korrigierte Fassung/Corrected Version/Version corrigée

EP 0 464 307 A1

The present invention relates to a process to improve the performances and to reduce the corrosion effects in high pressure and temperature condensation of the NH3, CO2, H2O vapours, which are generated in the treatment systems, so-called of stripping, of the solution coming from the urea reactor, said condensation being carried out by means of a carbamate condenser in particular of the tube bundle "Kettle" type to which part of the carbamate solution effluents from the condenser itself is recycled.

As known in modern urea plants characterized by the isobaric stripping of most of the unreacted substances contained in the urea solution outflowing the reactor and which utilize as stripping agents part of the CO2 or NH3 feed stream, the so-obtained stripping vapours are condensed in suitable heat exchangers recovering the heat produced in said condensation with low pressure steam production (4÷5 bar a).

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Methods have been proposed, for example in the second integration of the Italian Patent Application No. 23214, in which is described a horizontal tube bundle condenser with recirculation outside the condenser of part of the carbamate solution effluent for the same apparatus this system being studied to solve the critical aspect of mixing of the absorption liquid and the vapors to be condensed in order to ensure an optimial distribution (steeping) of the liquid-steam mixture on the inside of the pipes of said condenser, that only partially and in an insatisfactory way solve the problems present in the above mentioned equipment.

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